

STAT

PHOTOELECTROCHEMICAL EFFECT OF PHTHALOCYANINS, CHLOROPHYLL
AND PHEOPHYTIN

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^{appearance} ^{on}
The ~~rise~~ of a photopotential ^{on} in an illuminated electrode bearing a film of pigment and placed in an electrolytic solution is in direct relation with the photochemical, oxidizing-reducing reactions in which the pigment molecules take part. (1)

In connection with the significance of oxidizing-reducing processes of photosynthesis, it seemed interesting to investigate the photoelectrochemical behavior of water-insoluble chlorophyll and its related compounds pheophytin and phthalocyanin ^{as well as} with its magnesium complex, the photochemical reactions of which were the subject of a ^{many-sided} multilateral study in the photobiochemical laboratory of the Biochemical Institute imeni A. N. Bakh. (3)

(Z. Ye. Lobanova has made certain preliminary measurements, in the laboratory of A. N. Terenin, Physics Institute of the Leningrad University, of the photoelectrochemical effect ^{produced by} in connection with a film of magnesium phthalocyanide ^{deposited on} furnished by the photobiochemical laboratory and electrophoretically spread over platinum. The Mg phthalocyanin was furnished by the photochemical laboratory.)
Fig. 1 shows the diagram of the apparatus used in our experiments.

(Fig. 1 -- Diagram of apparatus. 1) Cine--lamp: 300 watts.
2) Condenser. 3) Light filter absorbing infrared rays. 4) Light

filter. 5) Platinum electrode. 6) Electrolyte. 7) Saturated solution of potassium chloride. 8) Cock. 9) Calomel electrode. 10) Lamp potentiometer (sensitivity, 1--2 millivolts).

When experimental conditions required the pumping out of air, we used a ^{measuring vessel} gauging-device formed by a quartz vacuum tube with two platinum electrodes. In this case one of the platinum electrodes, kept in the dark, served as standard.

We used the following as materials for the experiment:
1) chlorophylls (A+B), (A) and (B), obtained in our laboratory by the chromatographic method of separation; 2) pheophytin, obtained by the action of acid on chlorophyll or, directly, from nettle, after Fisher; 3) phthalocyanin and its magnesium complex in the form of crystalline powders.

The following methods were used to ^{deposit} spread the films on the electrodes: 1) electrophoretic; 2) evaporation of ether solution; 3) vacuum sublimation (only for the phthalocyanines).

As a result of the experiments we established that, as a rule, the potential of the inert electrode covered with a film of any of the tested compounds and immersed into an electrolyte, changes under illumination, i. e., that these compounds show a photoelectrochemical effect.

According to V. I. Veselovskiy (3), not simply the potential which rises with time, but the ^{rate} speed of the change of potential under the action of irradiation must serve as the basic characteristic of the photoelectrochemical process. However, for the

given materials, the ^{rate} speed of establishment of a stationary ~~sig-~~
^{value} ~~nificance~~ of the potential ~~-----~~ ^{is great} ~~[illegible]~~ ^{an approximate} ~~i.e.,~~
~~in Russian text~~ one can say, in a ~~close~~ ^{an approximate} treatment of the phenom-
 enon, that the intensity of the stationary photopotential (php) is
 in direct dependence ^{on} from the initial photocurrent. ✓

Fig. 2 shows the change of potential curves obtained with
 and without light from the chlorophyll films; fig. 3, from the
 pheophytin films; and fig. 4, from the phthalocyanin films placed
 in a neuter solution of potassium chloride.

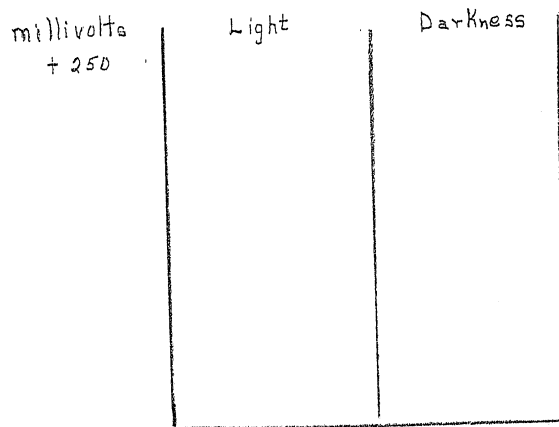


Fig. 2 -- Change in time of the potential of a chlorophyll film
 obtained by evaporation of an ether solution. The electrolyte is
 2NKCl. Effects with and without light are shown.

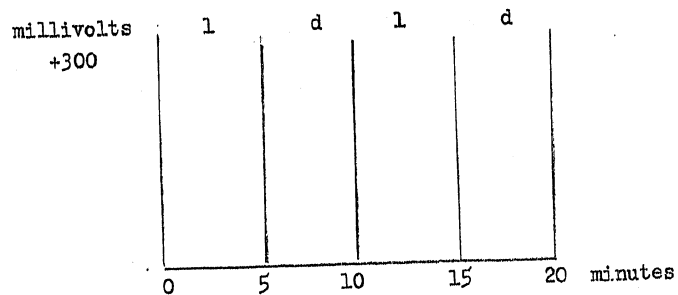


Fig. 3 -- Change of potential with a pheophytin film obtained through electrophoresis. The electrolyte is 2NKCl. Light is turned on and off every five minutes.

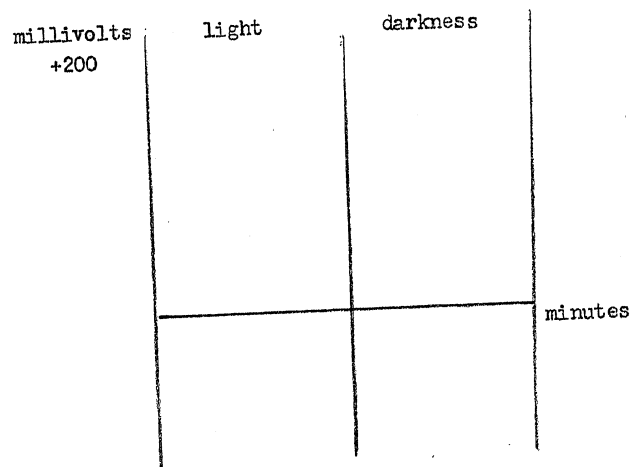


Fig. 4 -- Change of potential in time for a phthalocyanin film obtained by sublimation in vacuum. The electrolyte is 2NKCl+O,1NKOH. Light is turned on and off.

As appears from the curves, the potential of the illuminated electrode shifts to the positive side with all the compounds except pheophytin which, under such experimental conditions, shows a negative php.

Measurements under differently lit films showed that the php is proportionate to the intensity of absorbed light.

The illumination of the films with lights of different wave length, separated by means of a light filter and Beckmann's monochromator showed that the spectrum of photoelectrochemical action corresponds to the absorbance spectrum of the films in the visible and near ultraviolet sector of the spectrum.

In specially conducted experiments (with illumination of the blackened side of the electrode opposite to the film) it appeared that the observed film php is not a consequence of the heating of the film by the absorbed light energy.

The spreading of double strata of pigments producing phps of different signs in a given electrolyte, made it possible to establish that the photoelectrochemical effect is determined by a superficial interaction between the film and the electrolyte and is not localized on the surface of the electrode.

The sign and the intensity of the php is closely connected in the tested pigments with the oxidizing-reducing property of the electrolyte surrounding the film. In the presence of oxidizers, particularly of air oxygen, one usually observes a positive php connected with the presence of photo-oxidizing pigments (in certain

cases pheophytin is an exception). The presence of neuter salts in the solution does not have much significance in this case.

The role of oxygen in the rise of a php is confirmed by experiments where air was removed from the electrolytic solution. The pumping out of air provokes a sharp and significant drop in the positive php. If we introduce into the electrolyte such a typical oxidizer as quinone, the pumping out of air does not lead to a significant drop in the php. This shows that quinone can substitute dissolved oxygen.

In the presence of reducers like Na hydrosulphite, Na sulphite, hydroquinone and ascorbic acid in the conditions where the reducing qualities of these manifest themselves, the positive php either diminishes strongly, or changes its sign to negative, which testifies to the presence of an electron shift corresponding to the photoreduction of pigments.

It should be noted that, when using alcoholic instead of aqueous solutions, the same results were obtained both regarding the intensity and sign of the php and the role of oxidizers and reducers. Experiments with alcohol could, of course, be conducted only with phthalocyanins, for chlorophyll and pheophytin are both easily soluble in alcohol.

✓ This shows that not the medium, but the ^{neutra} neuter molecules dissolved therein, like O₂, quinone, ⁴hydroquinone and others, and also the ions with oxidizing and reducing functions are basically significant in the rise of a php.

The pH of the medium also has a definite influence on the photoelectrochemical effect of the tested pigments. In this sense one can note a definite difference in the ^{behavior} conducts of phthalocyanines on one side and of chlorophyll and pheophytin on the other.

The php of phthalocyanines in an alkaline medium and in the absence of reducers was always positive and stronger in intensity than in an acid medium. The change of potential happened faster than with acid and the ^{limiting} top potential was reached very fast both with and without the admittance of light.

In the case of chlorophyll and pheophytin, the ^{sign} change of the potential ^{change} sign under illumination and in an alkaline medium was, as a rule, negative. This fact is probably connected with the easier reducibility of these compounds in the presence of bases, a fact that was discovered earlier in the photobiochemical laboratory.

Very interesting is the difference in conduct of chlorophyll and pheophytin under identical conditions. These compounds either show a php of different sign, as happens when solutions of ^{neutral} neutral salts are used as electrolyte; chlorophyll then has a positive php, and pheophytin a negative one. Or else, if the php sign is the same, negative in an alkaline medium and positive in an acid medium, then the positive photopotential is always considerably higher with chlorophyll, while the negative one is higher with pheophytin. This compares well with the data obtained earlier (4) in regard to the easier photoreducibility and the more difficult photo-oxidizability of pheophytin over chlorophyll and, consequent-

ly, in regard to the possible role of a central atom of magnesium in these processes.

All the phenomena described above were produced with pigment films spread over carbon or graphite electrodes, but the absolute php values were considerably smaller and, as a rule, even for the phthalocyanins, did not surpass a few millivolts. No php could be observed on these electrodes without the presence of films.

On the basis of obtained data one can affirm that the measuring of photoelectrochemical potentials is a valuable method of study of the photochemical properties in the tested pigments and will have to be adopted in the future as the simplest and perhaps the only way of solving a series of problems connected with the oxidizing--reducing function of chlorophyll during the primary ----- [illegible in Russian text] photochemical process of photosynthesis.

There is no doubt that a further development of this method and its application to the research on heterogeneous photochemical reactions of the protein complexes of chlorophyll is the order of the day.

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QUOTED LITERATURE

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